

A Review Article on Uses, Effects & Implications of Fly Ash Due To Its particle Size & Unburned Carbon

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ABSTRACT

Fly ash is a particulate matter ranging in size from 0.01 to 100 μm released into the flue stream during combustion of coal in power generating stations. The mineralogical, physical and chemical properties of fly ash depend on the type of coal, combustion conditions, emission control devices and handling methods. Chemically it is a mixture of oxides, hydroxides, carbonates, silicates and sulphates of calcium, iron, aluminum and other metals in trace amount. It is grey to black in color, abrasive, alkaline and refractory in nature. Fly ash is regarded as a pollutant due to its negative impact on the ecosystem, although it has alternate, safe and viable utilities [1]. Unburned carbon particles can be assumed to possess a work function equal to that of graphite (4.0 eV) and ash a work function equal to that of silica or alumina (SiO_2 : 5eV; Al_2O_3 : 4.7 eV) respectively [2, 2A]. The fly ash carbons occur in the residual coal ash as a result of the incomplete combustion process. Due to the increasing applications of activated carbons, this study has been focused on the preparation of cost-effective adsorbents as a substitute for activated carbon materials. The main objective of this study is to explore the possibility of using fly ash of different particle size in presence of unburned carbon as an adsorbent.

KEY WORDS: Unburned Carbon, Fly Ash, Adsorbent, Particle Size.

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I. INTRODUCTION:

Fly ash is a byproduct of coal combustion and it contains several mineral matters such as carbon, silica, alumina, iron oxide and sulfur. Unburned carbon in fly ash is a major index to determine the efficiency of coal combustion in a power plant. Fly ash with a high volume of unburned carbon indicates poor combustion efficiency of power plant, which results in a high emission of pollutants and higher fuel consumption. In order to ensure the combustion efficiency and maintain low unburned carbon content in fly ash, the power industry is constantly analyzing the most effective way to monitor the unburned carbon in fly ash. The mechanism of ash formation involves several particles that originate from a single coal particle through the initial process of fragmentation. As the combustible carbon matter surrounding the mineral components burnout, finely distributed ash components reach the particle surface.

The molten ash components merge into larger particles whereas some part of the ash vaporizes at high temperature, condense and coagulate. Vaporous pollutants and heavy metals accumulate over the ash particles. Coarse ash particles known as bottom ash (or slag), fall to the bottom of the combustion chamber due to its gravity, while the lighter fine ash particles called fly ash, remain suspended in the flue gas. In pulverized fuel firing systems, 70-90% is released as fly ash while 10-30% is removed as coarse-grained bottom ash [3]. A loss-on-ignition (LOI) test and thermo gravimetric analysis (TGA) are among the techniques being used to determine unburned carbon content in fly ash. Currently, the LOI technique is the standard method used in the industry. This method, however, wrongly assumes that oxidation of unburned carbon in fly ash is the only source of weight loss when the sample is heated in a furnace for several hours at 725°. This false assumption deteriorates the accuracy of the LOI measurement result [4]. On the other hand, TGA can provide very accurate result for unburned carbon in fly ash. It is, however, a very expensive procedure [5].

II. CHEMICAL COMPOSITION OF FLY ASH:

Fly ash consists of percentage of silica (SiO_2), alumina (Al_2O_3) and magnetite (Fe_2O_3) and other components as listed in Table 1, fly ash also contains oxides, hydroxides, carbonates, silicates and sulphates of different elements like phosphorous, potassium, calcium, magnesium, iron, manganese etc. The chemical composition of fly ash enables its use for the synthesis of zeolite, alum and precipitated silica [6]. Based on the nature of coal and combustion conditions, fly ash may contain various levels of heavy metals such as antimony, arsenic, barium, boron, cadmium, chromium, cobalt, copper, lead, mercury, molybdenum, nickel, selenium, silver, and zinc [7].

TABLE-1:
CHEMICAL COMPOSITION OF FLY ASH PRODUCED FROM DIFFERENT COAL TYPES [6]

| Sr. No. | Chemical Component (% by wt) | Coal Types, from which fly Ash is produced | | |
|---------|--|--|----------------|---------|
| | | Bituminous | Sub-Bituminous | Lignite |
| 1 | Silica (as SiO_2) | 20–60 | 40–60 | 15–45 |
| 2 | Alumina (as Al_2O_3) | 5–35 | 20–30 | 10–25 |
| 3 | Iron Oxide (as Fe_2O_3) | 10–40 | 4–10 | 4–15 |
| 4 | Calcium (as CaO) | 1–12 | 5–30 | 15–40 |
| 5 | Magnesium (as MgO) | 0–5 | 1–6 | 3–10 |
| 6 | Sulphuric Anhydride (as SO_3) | 0–4 | 0–2 | 0–10 |
| 7 | Sodium (as Na_2O) | 0–4 | 0–2 | 0–6 |
| 8 | Potassium (as K_2O) | 0–3 | 0–4 | 0–4 |

III. EXPERIMENT CARRIED OUT EARLIER:

A: The Influence of Unburned Carbon Particles on Electrostatic Precipitator Collection Efficiency [8]:

The test bench was comprised of one stage electrostatic precipitator (ESP) model chamber with a set of discharge and collecting electrodes, ESP inlet and outlet air ducts, dust particle feeder, high voltage supply unit (negative polarity) and exhaust fan [9].

Fly Ash Analysis:

Physical & chemical analyses of the fly-ash used in tests are given in table 2. Figure 1 shows results of fly ash particle size distribution.

Table-2: Properties of Fly Ash

| Parameter | Units | Fly ash type | | |
|------------------------------|-----------------|-----------------|-----------------|-----------------|
| | | G | A | K |
| Chemical composition of ash: | % | | | |
| SiO_2 | | 28.99 | 25.74 | 40.39 |
| Fe_2O_3 | | 3.67 | 5.91 | 10.01 |
| Al_2O_3 | | 17.14 | 24.31 | 18.09 |
| TiO_2 | | 0.86 | 1.24 | 0.96 |
| CaO | | 2.82 | 2.18 | 5.44 |
| MgO | | 1.01 | 0.50 | 1.47 |
| SO_3 | | 2.26 | 5.76 | 1.27 |
| K_2O | | 2.68 | 3.58 | 2.08 |
| P_2O_5 | | 0.01 | 2.10 | - |
| Na_2O | | 1.14 | 2.82 | 1.47 |
| Unburned carbon in ash: | % | 28.60 | 23.31 | 17.92 |
| Density | kg/m^3 | 2090 | 2320 | 1760 |
| Resistivity | ohm cm | 5×10^7 | 1×10^8 | 2×10^7 |

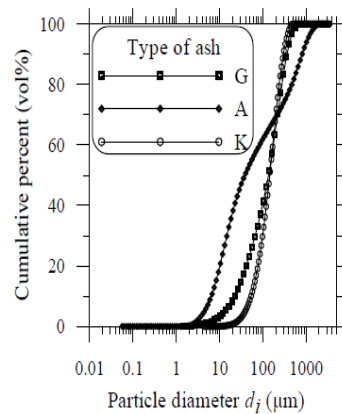


Figure 1. Particle size distribution of tested fly ashes.

The tested fly-ash samples coded as G, A and K characterize high unburned coal contents in a range of 18-28%. The measured fly-ash resistivity in laboratory conditions was 10^7 - $10^8 \Omega \times \text{cm}$ and remained almost steady with temperature changes from 20°C to 215°C. The particle size distribution of tested fly ashes was measured using a Mastersizers 2000 analyzer of Malvern Instruments, and the resultant distribution curves (figure 1) show characteristic shape of fly ashes from grate boilers.

Discharge Electrodes Configurations:

The discharge electrode (DE) shape and basic dimensions are depicted by figure 2 and voltage-current Characteristics of tested electrode configuration by figure 3.

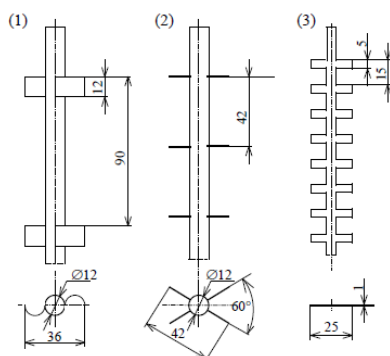


Figure 2. Design of the discharge electrodes, dimension in mm.

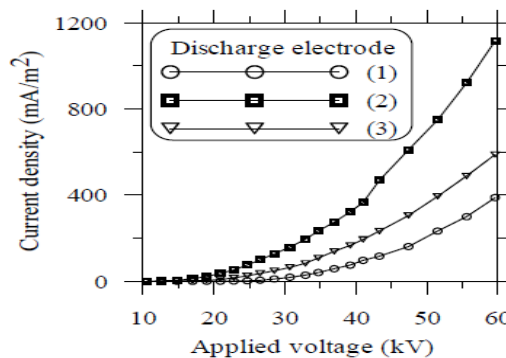


Figure 3. Current-voltage curves of discharge electrodes tested under clean air conditions.

The performance tests were conducted on a bench scale laboratory ESP with fly ash samples described in table 2 and figure 1. The test results are presented as a function of ESP applied voltage for different ash samples for discharge electrode type (2) and (3) respectively. For all tests the air flow velocity in the ESP was held constant at 0.8 m/s and the dust concentration at 0.2 g/m³. For each level of the supply voltage three collection efficiency tests were carried out.

The above observations show that besides the unburned coal contents of fly ash and its resistivity other factors also affect the precipitator collection efficiency. It calls on further investigation on such fly ashes with special consideration to its chemical composition and unburned coal content for respective particle size distribution ranges.

Laboratory tests have shown that the chemical composition of fly ash (in that unburned coal) as well as its size distribution has significant influence on the dust cleaning process. Likewise the design of discharge electrodes has shown a strong influence on the dust cleaning. Tests of precipitation efficiency were carried out on a laboratory electrostatic precipitator (ESP) model using fly ash samples of diverse size distribution and unburned coal content collected from several grate boilers. Test results show explicit dependency of the ESP precipitation efficiency on physical and chemical characteristics of the fly ash, design of discharge electrodes and amount of electrical energy delivered to the ESP. Mercury concentration measurements show higher levels in the fly ash than in the fired coal indicating high sorption capacity of the fly ash. Prior observation suggests good mercury adsorption on fine fly ash particles in the presence of elemental coal. Hence the improvement of ESP collection efficiency of fine particles containing unburned coal may help decrease the emission of mercury.

B: Size Distribution of Unburned Carbon in Coal Fly Ash and Its Implications [10].

A total of nine fly ashes, including five class F and four class C samples, have been selected from sample bank of roughly 80 fly ashes. These samples have been obtained from utilities (or ash brokers) throughout the US. The class F ashes are formally characterized by an inorganics content of ($\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$) which is no less than 70%, whereas the class C ashes must contain only more than 50% by weight of these components [11]. The difference between the two classes is associated with the higher alkali and alkaline earth contents of the class C ashes. This classification generally places the ashes from bituminous coals and anthracites into class F and those from lignites and subbituminous coals into class C. The actual samples are shown in **Table 3**. The particular utilities and units that produced the samples are not specifically identified, because not all samples are fairly representative of their current 'normal' practices. All samples were, however, produced in full scale boilers under what can be considered 'typical' utility operating conditions.

Table-3

Fly Ashes examined in this study

| Sample No. | Class | LOI (%) | Source |
|------------|-------|---------|-----------------------------------|
| FA21 | F | 6.1 | New England Utility 1: sample # 1 |
| FA22 | F | 33.6 | New England Utility 1: sample # 2 |
| FA24 | F | 2.7 | Midwest Utility: sample #1 |
| FA26 | F | 4.0 | Midwest Utility : sample # 2 |
| FA74 | F | 9.8 | New England Utility 2 |
| FA41 | C | 1.1 | Texas Utility |
| FA65 | C | 0.74 | Upper Midwest Utility: sample # 1 |
| FA66 | C | 0.92 | Upper Midwest Utility: sample # 2 |
| FA75 | C | 1.3 | Upper Midwest Utility: sample # 3 |

Fly ashes were mechanically sieved at room temperature in 150 g batches, following drying in a laboratory oven at 120°C. Standard US testing sieves were used (ASTM E-11) specification sieves 45, 75, 140, and 325, with nominal openings of 355, 180, 106 and 45 μm , respectively). Sieving was performed for 25 minutes, using a mechanical sieve shaker. Each collected fraction was weighed.

The amounts obtained in the smaller size cuts were sensitive to subtle differences in preparation conditions. The same separations, repeated on different days, could show variations of as much as ± 40 wt% (relative) in the $< 45\mu\text{m}$ and 45–106 μm cuts. This was due to differences in the extent of agglomeration of the finer particles in different runs. The larger particle fractions did not show such variation. Factors such as moisture and electrostatic charging (which would be sensitive to daily variations in the relative humidity of the air) influenced the agglomeration. The uncertainty introduced by this variation in separations at the fine end does not, however, have a significant impact on the general conclusions of this study because these did not depend very strongly upon assignment of the 'correct' masses to these smallest size fractions.

Adsorptive Capacity:

The nature of the porosity in a fly ash carbon plays an important role in determining its adsorptive capacity. Most fly ash carbon samples have a large amount of porosity, including micro pores (20 \AA), meso pores (20–500 \AA) and macro pores (>500 \AA), based upon the IUPAC classification. In order to determine the surface area and porosity of the fly ash samples, N_2 gas adsorption isotherms were measured at 77 K using an Autosorb-1 system from Quanta chrome Corporation. Samples were outgassed for several hours at 573 K in vacuum prior to adsorption measurements. At least 20 adsorption and 20 desorption points were obtained for each sample. Brunauer, Emmet and Teller (BET) theory [12] was used for calculating surface areas.

Carbon dioxide is an alternative adsorptive that finds wide use in the combustion community. It has been concluded that nitrogen is, however, the better choice of adsorptive for high burn-off chars [13, 14]. This is because carbon dioxide apparently has difficulty in filling the larger size range of micro pores, and the issues related to activated diffusional limitations are much less severe for high burn-off materials than for freshly prepared chars.

The inorganic fraction made a relatively constant contribution of roughly 0.7–0.8 m²/g in any ash. This contribution was determined by burning out all of the residual carbon in the sample, using a method similar to that for LOI determination, and then measuring the surface area of the ash without carbon. Generally, the carbon's contribution to the surface area was at least comparable to, and in many cases much greater than, the contribution from the inorganic part. When carbon surface areas are reported below, they have been calculated from the surface areas of the total fly ash less the inorganic contribution. The surface areas reported below are all specific surface areas, calculated as m² per gram of carbon in the sample.

The unburned carbon in coal fly ash is characterized by a broad size distribution. In class F ashes, the majority of the carbon is contained in ash fractions that are less than 100 μ m in size. There are a great many particles of submicron size. In class C ashes, it is also common to find a significant fraction of the unburned carbon as large, unburned char particles. The large unburned char particles that are found in either class C or class F ashes are typically quite mineral rich; the LOI of these particle fractions is in the range from about 20 to 60%. The finest fractions of the ash, and with that the fine particles, make the major contribution to AEA adsorption. This is for two reasons—the mass of fine carbon particles is greater than the mass of large carbon particles, and they offer greater accessibility to their adsorptive surfaces. The adsorptive surfaces are those near the external (geometrical) surface of the particles, and are those that can be accessed by AEA on the time scales of the foam index test. The class F carbons are characterized by significantly lower specific surface areas than are the class C carbons, but their relative AEA adsorptive capacities per unit surface are quite comparable. This is why a certain amount of unburned carbon in a class C ash may be perceived as considerably worse than the same amount of unburned carbon in a class F ash. Still, there is not a perfect correlation of adsorptive capacity with total carbon surface area. Again, this is because a large amount of surface area, contained in large unburned carbon particles in class C ashes, is relatively ineffective for adsorption presumably due to accessibility limitations.

C: Effect Of Fly Ash Particle Size On Its Capacity To Neutralize Acid Mine Drainage And Influence On The Rheological Behaviour Of Residual Solids [15].

Fly Ash from South African Power station was successfully used to treat Acid Mine Drainage (AMD) and the insoluble residue solids that were obtained as a result of reaction between fly ash and Acid Mine Drainage proved suitable as backfill materials for mine stabilization. Particle size Distribution (PSD) of fly ash varies from time to time depending on coal burning conditions in the power stations. Variability in particle size distribution and fly ash could influence its capabilities to neutralize AMD as well as flow behavior of residual solids that have to be transported to the backfill site. The objective of this paper was to study the influence of particle size distribution on the above mentioned properties.

Particle size analysis showed that the fly ash distribution was as given in table -4 below.

Table-4

| Sr. No. | Particle size | Characteristic |
|---------|---------------|---|
| 1 | < 25 μ | 38 % passing from 25 μ sieve. |
| 2 | 25 – 75 μ | 42 % (passing from 75 μ sieve and retaining on 25 μ sieve) |
| 3 | 75 -150 μ | 14 % (Passing from 150 μ sieve and retaining on 75 μ sieve) |

It was observed that the particle size distribution of fly ash has influence on the neutralization reaction time and also on the removal of efficiency of toxic elements and sulphate concentrations. The smaller particle size fraction enhances neutralization kinetics due to the higher reactive surface area increases the slurry viscosity. Anomalous behavior was observed for samples enriched with respect to the coarse particles. Therefore the degree of dewatering necessary for obtaining the desired flow characteristic of the slurry composed of the residual solids would be dependent upon the particle size of the fly ash utilized during neutralization.

D: Effects Of Adsorbent Dose And Particle Size On Adsorption Of Reactive Textile Dyes By Fly Ash [16].

The fly ash was obtained from Afsin-Elbistan Thermal Power Station in Turkey. The Afsin-Elbistan power plant consumes 18×10⁶ metric tons of coal per year and generates about 3.24×10⁶ metric tons of fly ashes returning to the dumping area of the mine as combustion waste. The particle size distribution of the fly ash was found between 3.6 and 181 µm. Higher percentage of the fly ash consists of Particles with diameter 40–125 µm (determined by the method of laser beam dispersion using the Malvern 2000 particle size analyzer). The particle size of the adsorbent was determined by sieve analysis. The fly ash was sieved by using a sieve set and then was collected in the range of 40–50, 50–60, 60–80, 80–100, and 100–125 µm, respectively. The surface area of the fly ash was measured by BET (Brunauer–Emmett–Teller nitrogen adsorption technique). The bulk density of the adsorbent was determined with a densitometer. The fly ash was used as received without any pretreatment in the adsorption experiments.

Batch adsorption tests were conducted by varying adsorbent particle sizes and adsorbent doses on a rotary shaker using 100 ml screw-cap conical flasks containing 50 ml of dye solution having a concentration of 100 mg/L, pH 6, and agitation speed of 250 rpm and temperature of 22°C for a period of 48 h. After this period, the final equilibrium concentrations of the dye in solution were measured spectrophotometrically at a wavelength of 518, 585 and 411 nm for RR, RB and RY, respectively using a Perkin-Elmer UV-visible spectrophotometer model 550S. The percentage removal of dye, p , was calculated using the following equation

$$p = \frac{(C_0 - C_e)}{C_0} \times 100$$

Where, C_0 and C_e are the initial and equilibrium dye concentration (mg/L), respectively. All experiments were replicated and the average results were used in data analysis.

The adsorption of three reactive dyes, Remazol Red, Remazol Blue and Rifacion Yellow, from aqueous solutions using fly ash as an adsorbent was studied in an agitated batch system to investigate the influence of two parameters viz., adsorbent dosage and particle size on the removal efficiency of the reactive dyes. Firstly, the adsorbent was characterized with using several methods such as SEM, XRD and FTIR. The FTIR suggested that the dye on fly ash is probably indicating fly ash/dye complexation. XRD pattern of fly ash consisted of mainly quartz, mullite with some magnetite and calcite. Surface morphology of fly ash and dye loaded fly ash were obtained with SEM. Secondly, the percentage of dye removal at equilibrium, p , was determined with respect to these two parameters with a constant initial dye concentration of 100 mg/L, agitation speed of 250 rpm, pH 6 and temperature of 22°C for a period of 48 h. The experimental data were treated with two simple empirical models used for predicting the percentage of the dyes adsorbed on the fly ash. Both models showed good correlation coefficients but the best model which determined the p values can be selected on the basis of the standard deviation of the calculated and experimental values.

Adsorption has been used extensively in industrial processes for separation and purification. In wastewater treatment, commercially activated carbon has long been used as a standard adsorbent for color removal. In spite of its widespread use in various cleaning procedures, activated carbon remains expensive; therefore, the development of low-cost alternative adsorbents has been the focus of recent research [17,18]. Contributions in this regard have been made by many researchers who have utilized a number of substances such as agricultural wastes: coir pith, banana pith, sugar cane dust, sawdust, activated carbon fibers and rice hulls [19–23], industrial solid wastes: fly ash, red mud and shale oil ash [24–31], and so forth.

IV. CONCLUSION:

Various studies have been carried out for uses, effects and implications of fly ash for its different characteristics. It has been established as an adsorbent for hazardous chemical compounds such as heavy metals, dyes & etc. however comprehensive study is required to establish its adsorption capacity based on its various particle size in the presence of unburned carbon in it. The effectiveness of its adsorption capacity in terms of level of separating contamination of for particular element need to be focus of further study.

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